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CONTENTS

		Page
I.	*The Measurement of Hydrostatic Pressure to 30,000 kg/cm².* By P. W. Bridgman	1
II.	*The Linear Compression of Iron to 30,000 kg/cm².* By P. W. Bridgman	11
III.	*The Compression of 46 Substances to 50,000 kg/cm².* By P. W. Bridgman	21
IV.	*The Elastic Scattering of Fast Electrons by Heavy Elements.* By J. H. Bartlett and R. E. Watson	53
V.	*Fossil Parasitic Hymenoptera of the Family Scelionidae from Baltic Amber.* By C. T. Brues	69
VI.	*Records of Meetings, 1938–40; Biographical Notices; List of Members; Statutes and Standing Votes*	91
VII.	*A Revision of the Nearctic Hemerobiidae, Berothidae, Sisyridae, Polystoechotidae and Dilaridae (Neuroptera).* By F. M. Carpenter	193
VIII.	*Photographic Evidence on the Visibility of Color Patterns in Butterflies to the Human and Insect Eye.* By C. T. Brues	281
IX.	*The Approximate Solution of Singular Integral Equations Arising in Engineering Practice.* By F. B. Hildebrand	287
X.	*The Inner Chapters of Pao-P'u-Tzŭ.* By T. L. Davis and Chên Kuo-fu	297
XI.	*An Experimental Study of the Absolute Temperature Scale. VI–IX.* By J. A. Beattie and others	327
XII.	*Freezing Parameters and Compressions of 21 Substances to 50,000 kg/cm².* By P. W. Bridgman	399
XIII.	*Pressure-Volume Relations for 17 Elements to 100,000 kg/cm².* By P. W. Bridgman	425
XIV.	*Records of Meetings, 1940–42; List of Members; Statutes, etc.*	441

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Vol. 74, No. 1, P. 1-10—October, 1940

THE MEASUREMENT OF HYDROSTATIC PRESSURE TO 30,000 kg/cm²

By P. W. Bridgman

Investigations on Light and Heat made and published with aid from the Rumford Fund.

(Continued from page three of cover)

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Presented Oct. 11, 1939. Received Oct. 13, 1939.

TABLE OF CONTENTS

Introduction 1
Instrumental Details 2
Corrections for Distortion 3
The Material for Transition 5
Determination of the Fixed Points 5
The Manganin Gauge 8

Introduction

A part of the problem of the extension of the controllable pressure range from 12,000 kg/cm² to 50,000 for certain phenomena and to 30,000 for others, a problem on which I have been engaged for the past few years, is to provide some method for the accurate measurement of pressure in the new range. For such phenomena as polymorphic transitions high accuracy in the measurement of pressure is not of extreme importance, but for those phenomena whose chief interest lies in departures from linearity with pressure, such as compressibility or change of electrical resistance, a higher degree of precision in the measurement of pressure is obviously desirable.

In the range of my earlier work, mostly up to 12,000 kg/cm², pressure was usually measured in terms of the change of resistance of a coil of manganin wire.[1] Before the resistance changes could be accepted as a satisfactory pressure indicator a preliminary study was made of the change of resistance against an "absolute" gauge of the free piston type. The resistance change of any one coil of wire proved to be linear in the pressure within 0.1 per cent up to 13,000 kg/cm², but different coils cut from the same spool might differ in their constant of proportionality by 2 or 3 tenths of a per cent, and coils from different manufacturers might differ by several per cent. A calibration of each individual coil in terms of some easily reproducible standard which determines a pressure fixed point was therefore indicated. For this fixed point the freezing pressure of mercury at 0° C. has been used in all my work; this pressure was found by original measurement against the piston gauge to be 7640 kg/cm².

In work already published[2] up to 30,000, and also in some earlier work to 15,000 and 20,000, pressure has been measured with a manganin gauge, by linear extrapolation of the constant determined at 7640. There was various evidence that any error in such an extrapolation could not be large, but now that I have started on a measurement in this range of the compressibilities of the relatively incompressible metals the time has obviously come to make the measurement of pressure as precise as possible. One would naturally first try to merely extend the former procedure to higher pressures, but this is not feasible because the free piston gauge had about reached its limit at 13,000, due to rapidly increasing viscosity of the pressure transmitting medium, demanding forces to rotate the piston great enough to break it, and also due to the rapidly increasing distortion, the correction for which can only be calculated by the methods of the theory of elasticity in a range in which the fundamental assumptions of the theory are becoming rapidly inapplicable. However, the fundamental idea of the free piston gauge, namely the measurement of pressure by measurement of the thrust on a piston in equilibrium with the pressure, appears to remain the simplest and perhaps the only method. The errors to which this is subject are two: those arising from friction and those arising from geometrical distortion. If these two sources of error could be overcome, then an extension of the same procedure as before could be used, namely direct measurement of some easily determined pressure fixed point against which the manganin gauge could then be calibrated and used thereafter as a secondary gauge. This is the course adopted in the following. By suitable design of the apparatus the friction has been cut down to a low figure; the corrections due to distortion have been determined by direct measurements of the interior bore of the apparatus while under pressure; the pressure of a suitable transition between solid phases has been determined as a pressure fixed point; and the manganin gauge has been calibrated in terms of these, and its departure from linearity determined. A variant of the former arrangement is that now the piston on which the thrust is meas-

ured is in direct contact with the solid undergoing transition, with no liquid as intermediary; in this way the problem of leak past the piston is minimized.

Instrumental Details

The chief frictional resistance to the motion of a piston arises at the periphery of the piston, in the packing; other things being equal it is proportional to the ratio of the active area of the packing material to the area of the piston. This ratio can obviously be cut down by making the ratio of periphery to piston area small, and by making the packing as thin as possible. There is then an advantage in working on a large scale, because the larger the scale the smaller the ratio of periphery to piston area. The diameter of the free piston formerly used to 13,000 was only 0.0625 inch; for this work up to 30,000, 0.5 inch was used. In fact, the cylinder containing the material undergoing transition, the piston, and the presses for pushing the piston, were the same as previously used in measuring the effect of pressure on resistance up to 30,000, and have already been sufficiently described.[2] The ½ inch piston producing the high pressure is pushed by a 3.5 inch piston, thus giving a multiplication of 49. The 3.5 piston is actuated by a hand pump connected to a calibrated 0.25 inch free piston gauge, similar to that used in much of my previous work. The pressure on the 3.5 piston does not rise above 10,000 lb/in^2, so that the weights on the 0.25 free piston gauge do not get above 500 pounds, which is easily manageable. Friction occurs both on the 3.5, and mostly on the 0.5 inch piston. Friction on the 3.5 inch piston is cut down by making the bore of the cylinder of the press as smooth as possible, and by using for packing material a disc of "Duprene" only 1/16 inch thick, instead of the ¼ inch thickness usually employed. The Duprene is held between brass discs ⅛ inch thick, which are a smooth sliding fit for the hole. The life of the packing is naturally cut down by using only 1/16 inch thickness, but it nevertheless is long enough to permit measurements with no inconvenience on this score. With these dimensions, the ratio of packing area to area of the piston is only 0.07.

The 0.5 high pressure piston was of carboloy, as in all this work. I am very much indebted for it to the Carboloy Company. This piston was made 0.010 inch smaller than the hole, so that there is no friction at the carboloy, but only at the end, where it pushes a packing disc against the solid undergoing transition. The construction of this packing disc is indicated in Figure 1. It consists of a disc of hardened steel, an easy push fit for the hole, and only 0.020 inch long on the straight part, bevelled below to an angle of 45° and pushing a conical packing ring of either beryllium-copper or phosphor-bronze, itself 0.035 inch thick. The endeavor is to make the thickness of the packing ring as small as is compatible with its not blowing out past the hardened steel disc.

Another most important factor in determining friction is the length of the slug of material undergoing transition. Before the transition occurs

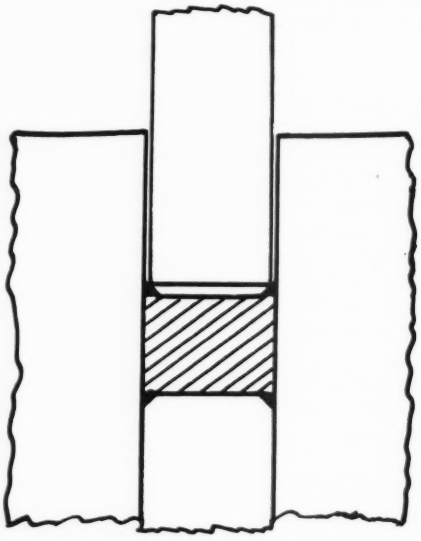

Figure 1. Method of packing the substance undergoing transition so as to give minimum friction.

there is of course appreciable volume compression of this material, which demands that the material slide in an axial direction along the walls of the container. This sliding is accompanied by friction, which resists the propagation of pressure, so that the pressure in the lower end of the slug is less than that in the upper end immediately under the moving piston. The material immediately under the piston may therefore be undergoing transition while that at the lower end is still below the transition pressure. There is the converse situation when the transition is approached from the other side, with release of pressure. The difference of pressure between the top and bottom increases exponentially with the length of the slug. Furthermore, after every change of pressure the

volume does not immediately take up its final value, but there is a frictional creep, which simulates the transition, and which rapidly becomes more important the longer the slug. Because of these two effects a large amount of material, that is, a long slug, is disadvantageous, but on the other hand, the greater the amount of material, the greater the volume change during the transition, and therefore the greater the ease of following the course of the transition and making measurements. The solution is to be found in decreasing the amount of material and at the same time increasing the sensitiveness of the method of measuring piston displacement, and also, of course, in using a transition with as large a volume change as possible. In this work the volume change of the material used, bismuth, is about 5 per cent, the length of the slug was only 0.375 inch with a diameter of 0.5 inch, and the piston displacements were read with a 0.0001 inch Ames dial gauge, which is sensitive to 0.00001 inch by estimation of tenths of the smallest divisions. Even with this favorable combination, frictional creep after every change of pressure is perceptible; one cannot be sure that the transition is running unless the creep exceeds something of the order of 0.0001 inch per minute.

Corrections for Distortion

The containers used in determining the fixed points were the regular "cylinders" used in previous work to 30,000. It will be remembered that these are somewhat tapering on the outside, and that simultaneously with the development of internal pressure they are pushed into a tapered collar fitting the outside, thus producing an external pressure which rises simultaneously with the internal pressure. The cylinder thus remains entirely within the elastic range and shows neither creep nor permanent alteration of dimensions after exposure to pressure. It is formally possible to calculate the change of cross section, but the calculations could be only approximate even if the equations could be solved exactly, because the boundary conditions are not well defined. Furthermore, the stresses are so high that deviations from the linearity assumed in elasticity theory may be suspected to be perceptible, so that some experimental check, even if rough, on the calculations is desirable.

There seems to be no easy method of measuring the change of internal dimensions of the container while the transition is running, but it is possible to determine, as a function of pressure, the change of internal diameter of a similar container filled with a liquid, as in the previous measurements of change of resistance under pressure, instead of a solid. This was accomplished by a modification of the sliding wire method of measuring small changes of length already extensively used in measuring compressibilities. A forked spring, shown in Figure 2, pressing against the

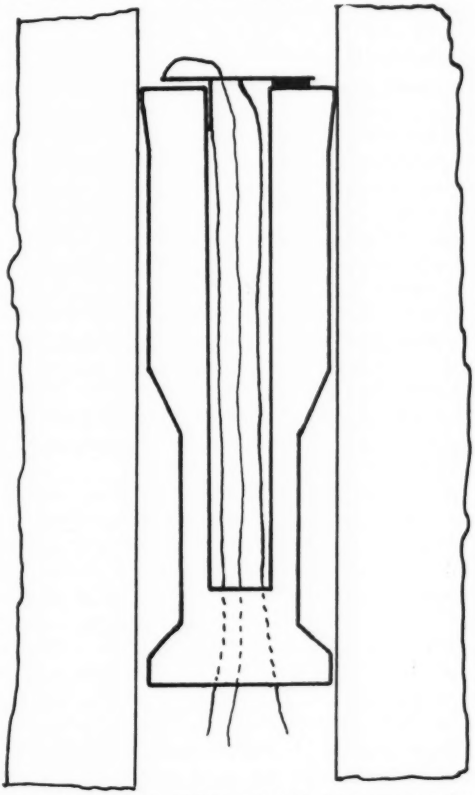

FIGURE 2. The sliding contact arrangement for measuring the change of internal diameter while under pressure.

walls of the container, carries across its end a transverse high resistance wire, fixed to one tine of the fork and sliding over a contact fixed to the other. Measurement with a potentiometer of the potential difference between fixed and sliding contact when a known current flows through the wire affords the method of determining small changes of dimensions. A number of small corrections are involved in reducing the measured potential differences to displacement; these had been previously determined.

A number of different set-ups were made with the apparatus for measuring distortion; most of the runs were incomplete because of one accident or another, but finally enough partial readings were obtained to give a satisfactory characterization of the behavior over the entire range. It is to be expected that the distortion of the bore of the cylinder will not be uniform along its length, being a maximum at the center of the stressed region, and a minimum at the ends, including the moving piston, where support is afforded by the parts of the cylinder walls not exposed to internal pressure. An attempt was made to find the distortion immediately under the moving plug by mounting the fork so that the cross wire is almost in contact with the lower end of the moving plug. In this arrangement the fork slides along the cylinder axis, pushed by the piston as it advances to increase the pressure. On release of pressure the fork is left standing in its extreme position. Measurements with increasing pressure therefore give the distortion at the moving plug, and measurements with decreasing pressure approximately the distortion at the center. Or the distortion at the center can be obtained both with increasing and decreasing pressure by placing the fork initially at the center.

The distortion determined in this way was in every case linear with pressure within limits of error. The distortion at the moving plug turned out to be 2/3 of that at the center. It may be shown theoretically, by an application of Betti's reciprocal theorem, that the distortion at the *packing* of the moving plug should be only one half the distortion at the center, where it is a maximum, assuming conditions for a semi-infinitely long thick cylinder. That is, if it had been possible to measure the distortion at the packing instead of some distance away at the end of the plug, theory would demand a value ½ that at the center instead of 2/3 as found. It would seem that the discrepancy is sufficiently accounted for by the difference of location, and in the following the factor ½ was therefore used in calculating the correction at the packing, which determines the effective cross section of the piston. The correction so found is a 0.57 per cent increase in area at 25,000 kg/cm². The correction thus found has to be still further modified for the finite length of the slug undergoing transition, the correction determined under the experimental conditions above being for a semi-infinitely long cylinder. It would probably be difficult to calculate this correction exactly, but a rough graphical estimate may be made of it. The radial distortion of an infinitely long cylinder under the distribution of internal pressure indicated in Figure 3 can be

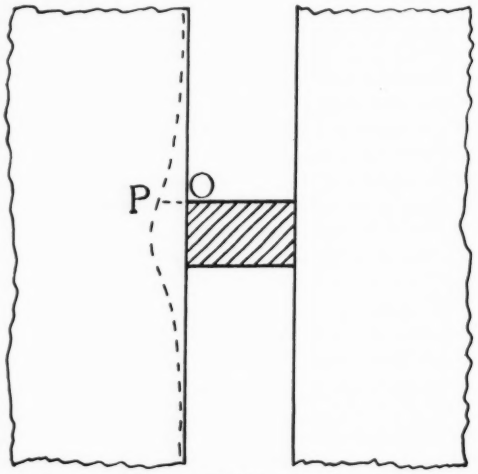

FIGURE 3. The dotted line indicates qualitatively the nature of the radial stretch at the internal wall under an internal pressure applied over the shaded region.

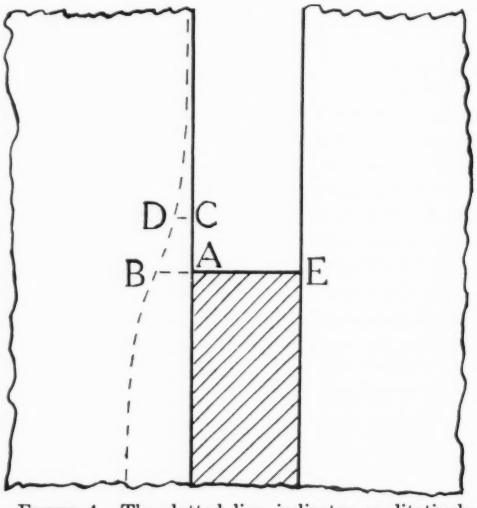

FIGURE 4. The dotted line indicates qualitatively the radial stretch at the internal wall under an internal pressure applied over the shaded region.

at once expressed in terms of the radial distortion of the same cylinder under the same internal pressure distributed along the whole of one semi-infinite axis as shown in Figure 4. If we assume for the latter that the radial displacement at a

point on the axis situated at a distance of one radius from the end of the region where the pressure ceases is one half the displacement at the place where the pressure ceases (that is, if in Figure 4 $DC = \frac{1}{2} AB$, where $AC = \frac{1}{2} AE$), a not unplausible assumption, then in Figure 3 the radial displacement OP is approximately 0.35 what it would be at the corresponding point in Figure 4. This makes the correction on the effective cross section of the piston 0.40 per cent at 25,000. The final correction for the cross section was taken as 0.5 per cent at 25,000. The uncertainty in the final result arising from uncertainty in this correction should not be more than 0.2 per cent at the most.

The correction can be calculated from the dimensions of the cylinder and the elastic constants with the simplifying assumptions that the cylinder is infinitely long and exposed to internal pressure over its entire internal length, that the external figure can be taken as cylindrical with the mean external radius instead of tapering as it actually is, that the external pressure can be taken as uniform over the entire external infinite length, and that the longitudinal compressive stress arising from the thrust which forces the taper into its external collar in order to generate the external pressure is uniform along the axis. With these assumptions the calculated internal radial displacement comes out two thirds of that measured. The agreement is perhaps as close as could be expected in view of the extremely rough approximations that had to be made for the calculation. The effectiveness of the external support given to the pressure vessel is shown by the calculation to be very high, the radial enlargement under the actual conditions being only 0.26 of what it would have been if there had been no external support. Of course the uncertainty arising from the correction for distortion is correspondingly reduced, a great advantage of the method.

A further rough and presumptive check on the calculations was obtained by measuring with a simple mechanical contrivance the change of internal diameter while the cylinder was exposed to external pressure only by thrusting it into its collar. The change of internal diameter calculated with the same simplifying assumptions mentioned above was 83 per cent of the measured change.

The Material for Transition

The demands on a transition adapted to serve for a pressure fixed point are exacting; it must occur at the proper pressure, the transition must run rapidly and with large enough change of volume for easy manipulation with both phases present, the transition should start in either direction with the minimum amount of super- or subpressing, and there should be little or no region of indifference. This latter means that when the two phases are in contact at a fixed temperature, pressure should automatically come to a single final value, no matter whether that value is approached from above or below. This requirement of no region of indifference is automatically met when the phases are liquid and solid, as in the former method of calibration against freezing mercury, but it is a very restrictive requirement on the phase change of solids.

There were available for selection some 65 or 70 substances whose phase diagrams have been mapped out up to 50,000 kg/cm². Most of these may be summarily ruled out, chiefly on the ground of too great sluggishness of transition or too wide a region of indifference. Of the entire list only three were found sufficiently promising for further examination: Cu_2I_2 with a transition near 15,000; KCN with a transition near 20,000, and Bi with two transitions in the neighborhood of 25,000. KCN was tried, but proved too sluggish and also to have an appreciable region of indifference. Cu_2I_2 was not tried, the measurements with bismuth having in the meantime shown that the mercury and bismuth fixed points would be adequate, but I do not believe that if Cu_2I_2 were tried it would prove any more satisfactory than KCN. Bismuth proved much easier to handle even than freezing mercury, and seems satisfactory in every way. The measurements of the rest of this paper are based on the use of bismuth. If in the future it should be necessary for someone else to use some other transition it would be worth noting that in some cases the secondary properties of the transition are very sensitive to impurity, so that it is not inconceivable that highly purified Cu_2I_2 or KCN could be used.

Determination of the Fixed Points

Determinations of the transition pressures were made with three different pieces of apparatus. Two of these were not as favorable as the third; the measurements with them must be regarded as in the nature of checks. Most of the measurements were made with the apparatus already used for a variety of measurements to 30,000. This is shown in Figure 5. External pressure on the pressure vessel is produced by thrusting it into a tapered collar with a 6 inch piston. Pressure on

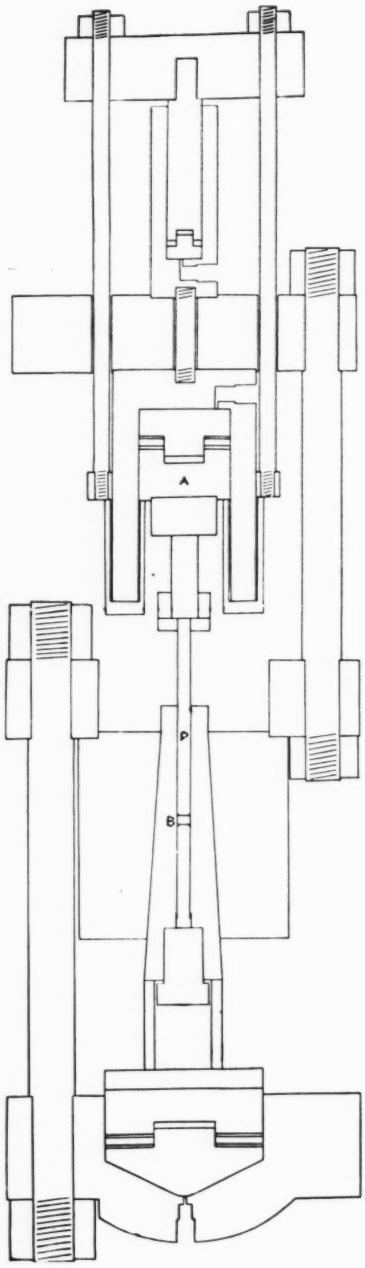

FIGURE 5. General view of the pressure apparatus. The bismuth undergoing transition is at B. In use the piston A is in a more extended position than shown, and the piston P is shorter.

the bismuth is produced by a 3.5 inch piston, driving a carboloy piston varying from 0.485 to 0.515 inches in diameter in the various set-ups. In order to be able to use the experimentally determined values for the correction to the cross section it is of course required that the external pressure on the vessel during the determinations of the transition be approximately the same as during the determination of the correction. This external pressure does not need to be controlled with high accuracy, however, and it was sufficiently good to measure the pressure on the 6 inch piston with a commercial Bourdon gauge of 15,000 lb/in^2 capacity. Friction on the outside of the cone could be allowed for by determining the displacement into the collar as a function of pressure, both with increasing and decreasing pressure. The pressure on the 3.5 inch piston driving the carboloy piston, on the other hand, has to be determined and controlled with the greatest possible precision. For this purpose the pressure on it was measured with a free piston gauge connected in series in the line between pump and press. The response of such a gauge to changes of pressure is always somewhat sluggish in spite of continual rotation of the piston, so that after every increase of pressure by operating the hand pump, or after every decrease by opening the valve, the pressure on the 3.5 piston would at first overshoot the mark, slowly creeping back to the final value as the piston gauge assumed control. Since the progress of the transition itself has to be judged by observing the creep, this effect might seriously lower the accuracy of the readings. It was avoided by providing a valve in the line between piston gauge and 3.5 inch piston, which was closed before every change of pressure, not being opened again until the piston gauge had become stationary. Even at constant pressure it was necessary to pump at intervals because of the unavoidable leak in the piston gauge. These intervals were made longer than they would have been otherwise by attaching a chamber of considerable capacity in the line, the volume compression of the liquid in this chamber providing a reservoir partially neutralizing the leak at the gauge. By this means the necessary pumping intervals were made longer than the intervals necessary to discover the direction of the transition, so that there was no complication on this score if the manipulations were properly made.

The bismuth had been highly purified by double electric deposition, and had furthermore been me-

chanically filtered in the liquid state and slowly crystallized.

The procedure in determining the transition pressure was first to increase the pressure in large steps on 3.5 and 6 inch pistons simultaneously, making rough measurements for orienting purposes of piston displacement and of the displacement of the pressure vessel into its collar. From this latter the friction could be calculated and thus a check made that such an external pressure had been attained as was required to duplicate the conditions during the measurements of the bore correction. Having arrived at the approximate pressure of the transition, the external pressure was kept constant by maintaining the pressure on the 6 inch piston constant, and the further manipulations were made only with the pressure on the 3.5 inch piston, the changes of which were slight. Pressure was now increased in small steps of approximately 400 kg/cm² on the bismuth, until the transition had started to run, as shown by the rapid piston displacement on the 0.0001 inch gauge. The total piston displacement corresponding to complete running of the transition was approximately known from previous work. The transition was allowed to run until it was one third or one half complete, and then pressure was lowered by 400 kg/cm², the transition then ceasing to run. Pressure was now increased again in steps of 80 kg/cm² (on the bismuth), pressure held at each point for three minutes, and the piston displacement noted during these three minutes as a function of time. There is always some creep after every change of pressure; the transition is shown by a larger creep which does not slow down with time. Having thus located the transition with increasing pressure, the reverse process was performed, giving thus a location of the transition with decreasing pressure to the nearest 80 kg/cm². With a little practice three minutes was sufficient to adequately characterize the creep and definitely establish the presence or the absence of the transition. The mean of increasing and decreasing determinations was taken as the transition pressure.

The ratio of the difference between increasing and decreasing pressure to the total mean pressure was defined to be the "total friction"; it includes ordinary mechanical friction and the natural width of the "band of indifference." The total friction varied considerably in the different set-ups. The minimum value was 2.9 per cent—this sets an upper limit to any possible region of indifference. The width of the region was established with much greater accuracy during the calibration of the manganin gauge, to be described presently. The question of whether the pressure determined by taking the mean of the increasing and decreasing pressures is the pressure of true thermodynamic equilibrium is after all of minor importance; the important point is how reproducible the mean is, and this question is answered by the consistency of the results with different set-ups. The results are summarized in Table I.

Rough check measurements were made with two other pieces of apparatus. One of these was the regular apparatus in which compressibilities are being measured to 50,000, to be described in fuller detail in another paper. The piston diameter of this is only 0.260 inch. The distortion correction was determined by calculation, allowing as well as possible for end effects, and at 25,000 was 1.35 per cent on the cross section. The other apparatus was a preliminary one of 0.40 inch diameter, which had been used in checking the effectiveness of giving external support to the cylinder by making it conical and pushing it into a collar. The external support in this apparatus was produced automatically by the thrust of the

TABLE I

PRESSURES OF THE I–II BISMUTH TRANSITION

30°			75°		
Diam. of Piston inches	Total Friction Per Cent	Pressure kg/cm²	Diam. of Piston inches	Total Friction Per Cent	Pressure kg/cm²
.4934	5.1	25,430	.5334	2.9	23,420
.5332	9.0	25,465	.4918	4.3	23,330
.5334	4.1	25,400	.4958	11.2	23,160
.4918	4.0	25,450			
.4958	7.4	25,380			
Weighted mean		25,420	Weighted mean		23,350

high pressure piston, and not independently. The external support on this is much less than with the two others, the external pressure being only 0.105 of the internal pressure, so that the correction for distortion is much larger. This correction was calculated to be 2.5 per cent for the middle of an infinite cylinder with the same simple assumptions as those already mentioned. This is to be reduced by an uncertain amount due to two end effects. Probably multiplication by a factor of one half is the best that can be done to allow for these end effects. The transition pressures found at 30° in this way with the 50,000 apparatus and with the early apparatus were 25,880 kg/cm² (total friction 8.2%), and 25,620 kg/cm² (total friction 4.5%) respectively. The agreement can probably be regarded as satisfactory in view of the more unfavorable dimensions of these two other forms of apparatus, and the larger calculated corrections.

In addition to the transition between the forms I and II, which is the one which has been just studied, bismuth has another transition between the forms II and III at pressures not much higher than I–II. With proper care the II–III point might also serve as a fixed point. The manipulations are somewhat less convenient, however, because in the first place the transition I–II has to be got out of the way before II–III can be measured, and the two transitions are so close together that this offers some inconvenience, and in the second place the volume change II–III is only two thirds that of I–II. I did not attempt therefore any determination of the transition II–III with an accuracy sufficient for calibration purposes, but I did make measurements with a single set-up with the good apparatus and obtained the following results: At 30°, 26,960 kg/cm² (total friction 4.5%); and at 75°, 25,850 kg/cm² (total friction 3.1%).

The Manganin Gauge

The fixed points having been established, the manganin gauge can be calibrated in terms of them. Two such gauges have been calibrated at this writing, wound from wire from the same spool. The manganin was of American origin, obtained from the Driver Harris Co., of 0.0035 inch diameter, double silk covered, wound non-inductively into coreless toroids of about 70 ohms resistance. Similar coils were used in measurements previously published of resistance to 30,000, pressure being obtained by linear extrapolation from the 7640 kg/cm² mercury point. The coils were seasoned by exposure for 8 hours per day for 6 days to a temperature of 140° C. with an interlude of 1 hour each morning at liquid air temperature, and also by several applications of 30,000 at room temperature. In general, the zero of these two coils has been noticeably more constant than that of other coils used in previous work to lower pressures.

The first coil was calibrated at room temperature (23° C.) against freezing mercury at 0° C. (7640 kg/cm²) in the apparatus with which most of my measurements to 12,000 have been made. In this apparatus the upper cylinder in which the coil is located is at room temperature, while the lower cylinder, containing the mercury, is at 0°. After this calibration the coil was transferred to the 30,000 apparatus, in which was placed a cylindrical slug of the same electrolytic bismuth as that whose absolute transition pressure was determined above, weighing about 28.5 gm. The rest of the 30,000 container was filled in the regular way with iso-pentane, which is known not to freeze at 30° below 30,000. From previous measurements the approximate transition pressure and the displacement of the piston to be expected during the transition were known. To facilitate following the progress of the transition the displacement of the piston was read with an Ames dial gauge graduated to 0.001 inch. The procedure was to raise pressure nearly to the transition point, wait for thermal and other equilibrium, then increase pressure sufficiently to start the transition, which was then allowed to run about one half to completion, as indicated by the piston displacement. Pressure was now reduced to such a value that there was no secondary reaction. From here as a starting point, and with the transition known to be one half completed so that the two phases were certainly in contact with each other, pressure was raised until it started to creep back perceptibly. This creep was allowed to continue until it had sensibly stopped, which might take from 10 to 15 minutes. The pressure reached in this way was called the equilibrium pressure from above. Pressure was next lowered until it started to creep up again, and in a similar way an equilibrium pressure from below was obtained. The mean of these two was taken as the equilibrium point. These two pressures differ by at least the true width of the region of indifference, but may differ by more than this because of sluggishness of the transition. If the width of the region of indifference were being

determined for itself a different procedure would be adopted. However, since pressure is here transmitted by a liquid, the pressures reached from above and below should not differ because of any factor of solid friction, and in fact the two pressures found with the manganin gauge calibrations are much closer than in the absolute determination of the transition pressures already described.

The first coil was calibrated against the bismuth I–II transition in this way at 26°, 30°, and 75°. The points at 7640 being already known from the measurements with freezing mercury (the 7640 point at 75° had to be obtained from previous measurements of the temperature coefficient), it was then possible to construct a second degree formula, giving pressure as a function of the measured displacement of the balancing point on the slide wire, reproducing the known points at 7640 and 25,000. If the relation were exactly linear, assumed in previous work, the second degree term would of course vanish. It did not vanish, but was small. At 30° the pressure of the bismuth point obtained by linear extrapolation from 7640 was 25,010 against 25,420 actual, or 1.6 per cent too low, and at 75° the figure was 23,120 against 23,300, or 0.8 per cent too low. The deviation from linearity is thus in an abnormal direction, shown by no other pure metal or alloy except single crystal antimony over a limited range.

The procedure in calibrating the second coil was somewhat different. In the first place, the 7640 point was experimentally determined at both 30° and 75° in order not to have to rely on the temperature coefficient determined on another sample. The 7640 point was determined in two steps. First, the 7640 point at room temperature of a coil of German manganin 0.0055 inch in diameter, such as had been used in all my early work to 12,000, was determined against freezing mercury at 0° in the regular way. The constant of this coil having been thus determined, the 30,000 coil was then compared against it at two temperatures, the German coil being kept fixed in one cylinder at room temperature, and the 30,000 coil in the other cylinder, which was thermostatically maintained first at 30° and then at 75°. The two coils were compared against each other at intervals of 2000 kg/cm² over the pressure range up to 12,000. The ratio of the resistance changes of the two coils proved not to be a constant, but there is a slight drift with pressure. A smooth curve was drawn through the points thus found, and the coefficient of the 30,000 coil at 7640 was taken from the curve.

The 30,000 coil was next transferred to the 30,000 apparatus for calibration at the higher points. The arrangements for this were modified as compared with those of the first calibration. The amount of bismuth was cut in two, and the space thus made available was filled with a thin walled steel shell containing mercury. In this way both mercury freezing points and bismuth transition points could be determined with the same apparatus. It was not feasible to cool the 30,000 apparatus to 0°; otherwise a single set-up could have been employed for the complete calibration. With this arrangement the mercury and the bismuth points were determined at 30° and 75°. The freezing pressures of mercury at these two temperatures are approximately 13,700 and 23,000 kg/cm². If the 13,700 point were accurately known, the 7640 point could be dispensed with. Theoretically, this point should be known from previous work, since the previous calibration of the manganin gauge against the free piston gauge had been made up to 13,000. Actually, however, the 7640 point was determined more carefully and a number of times, so that more confidence can be placed in it than in a value just beyond the previous range, it being well known that error is likely to pile up near the end of a range. At 75° the mercury point is in new territory, and is very close to the bismuth point; the determination at 75° is therefore to be taken in the spirit of a determination of a new fixed point.

At 30°, the bismuth point extrapolated linearly from 7640 was 24,910 instead of 25,420, or 2.0 per cent too low, against 1.6 per cent with the first coil. At 75° the linearly extrapolated bismuth point was 22,920 against 23,300, or 1.6 per cent too low, against 0.8 per cent of the first coil. This indicates that the departure from linearity of pieces of wire from the same spool may vary, just as the absolute constants are known to vary. The 7640 constant of the second coil was 0.6 per cent greater than that of the first one. This means that for the highest accuracy a two point calibration for every individual coil will be necessary. It would be too early to draw the conclusion that in general the greater departure from linearity goes with the greater first degree coefficient.

Two determinations at 30° of the bismuth point of the second coil on successive days gave identical results to the limit of sensitiveness of the readings, better than one part in 6,000. Determinations

of the bismuth and mercury points at 30° at an interval of two months gave an increase of 5/6000 of the bismuth point and 9/3700 for the mercury point. Taken at its face value, this would indicate a considerably larger secular change in the second degree term than in the first degree term, but it would be too early to draw this conclusion in general, because of the uncertainty in the bismuth point due to the region of indifference.

As a further indication of the variation in magnitude to be expected in the second degree term for different grades of manganin may be mentioned the results of the calibration up to 12,000 of the 30,000 coil of American manganin against the coil of German manganin. The ratio of the change of resistance of the first to that of the second varied approximately linearly with pressure from an initial value of 1.694 to 1.679 at 12,000. The interpretation of these results is that the second degree term in the German manganin is of the opposite sign from that of the American, the numerical value being such that a linear extrapolation by the German manganin from 7640 to 12,000 would be in error by 0.4 per cent at 12,000.

At 30° the measurements with the two coils gave values for the width of indifference for bismuth I–II varying from 60 to 100 kg/cm^2, and at 75° from 15 to 50. The lower of these values are to be taken respectively as upper limits for the true width of the region of indifference. In contrast to the bismuth points, the mercury points showed no perceptible region of indifference at all, the sensitiveness of the measurements being about 3 kg/cm^2. This is to be expected because of the different dynamics of a solid-liquid transition as compared with a solid-solid transition. In any event it affords a check on the sensitiveness of the method.

The following values were obtained for the melting pressure of mercury: at 30°, 13,700 and 13,730 kg/cm^2, and at 75°, 22,950 kg/cm^2. At 30°, the value of my former measurements, obtained by a slight extrapolation, was 13,610. At 75° I have already published[3] the value 22,570, obtained by a linear extrapolation of the manganin gauge. Correcting this by 1.6 per cent for lack of linearity of the manganin as determined above, gives 22,930, practical agreement with the present value. Extrapolation of my previous values from 20°, assuming a second degree relation in the temperature with the constants so chosen as to agree with the measurements in the range from 20° down to the atmospheric melting point, gives 22,600 at 75°. The melting line thus appears to have very slight curvature, but it continues in the normal direction over the entire range up to 75°. This is of some interest, because except for water, this is the highest pressure to which any accurate determinations of the melting parameters have been made. The curvature of the melting curve of water was also found to be normal, that is, the curve is concave toward the pressure axis.

Before the method of using the transition of bismuth to give fixed points was adopted, I made various attempts to calibrate the manganin gauge directly from measurements of the force driving the piston. This method was eventually abandoned in favor of the method above because it appeared that the friction on a piston packed to prevent leak of a liquid must always be greater than the friction of a piston packed against leak of a soft metal like bismuth. However, if the other better method had not offered itself, it would doubtless have been possible to obtain fairly satisfactory results by sufficient repetition of this method, since the curves with rising and falling pressure were surprisingly reproducible with different set-ups. The total friction with this method was 24 per cent at 25,000 and was rapidly becoming greater, so that I did not try for higher pressures. The measurements by this method showed the same abnormal departure of the resistance of manganin from linearity in pressure, and roughly of the same magnitude, between 1 and 2 per cent at 30° at 25,000, as by the better method above. It is worth while to have confirmation by this more direct method, even although the accuracy is lower.

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References

[1] P. W. Bridgman, Proc. Amer. Acad. 44, 201–217, 1909; 47, 321–343, 1912.

[2] P. W. Bridgman, Proc. Amer. Acad. 72, 157–205, 1938; 70, 71–101, 1935.

[3] First reference under (2), p. 192.